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PATENT SPECIFICATION (11) 1206501

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NO DRAWINGS

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(31) Convention Application No. W 43100 IVc/39b
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(54) PROCESS FOR THE MANUFACTURE OF NON-BLOCKING DISPERSIBLE POWDERS

ERRATUM

SPECIFICATION No. 1,206,501

Page 2, line 94, *for* 45 *read* 450

THE PATENT OFFICE
17th April, 1974

It has been proposed to improve the dispersibility by considerably increasing the amount of protective colloid in the dispersion before it is atomised. The addition of extra protective colloid before the end of the polymerisation has been suggested. Furthermore it has been recommended, in order to reduce the tendency towards blocking, either to add inert substances to the dispersions before they are atomised or to introduce inert substances into the powders during drying. When a small quantity of an inert substance is added the surface of the substance is, however, completely covered by the powder, so that an effective reduction of the tendency towards blocking cannot be achieved.

This invention provides a process for the manufacture of a non-blocking dispersible powder of a vinyl acetate polymer or a copolymer of vinyl acetate and at least one ethylenically unsaturated compound, the polymer or copolymer having a glass temperature below (down to −25°C). (Determination of the glass temperature, cf. Adhasion, 1966, 3, pages 97 to 100).

As polyvinyl alcohols with a saponification number of 60 to 255 it is possible to use water-soluble, partially esterified, for example, acetalised, polyvinyl alcohols or water-soluble saponification products of copolymers of a vinyl ester with at least one hydrophobic monomer that does not saponify under the conditions used to saponify the ester, for example vinyl chloride.

The polyvinyl alcohols preferably used in the process have a viscosity of 5 to 7 cps (4% by weight aqueous solution at 20°C) and a saponification number of 115 to 168. The polyvinyl alcohol is preferably added in a quantity such that the product after drying contains about 0.5 to 4% by weight of the polyvinyl alcohol. This makes it possible to maintain higher concentrations of the dispersions employed during atomising without

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(54) PROCESS FOR THE MANUFACTURE OF NON-BLOCKING DISPERSIBLE POWDERS

(71) We, WACKER-CHEMIE G.M.B.H., a Company recognized by German Law, of Postfach, Prinzregentenstrasse 22, 8 Munchen 22, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Dispersible powders can be manufactured by atomising a dispersion in a hot stream of air by means of a single-material or two-material nozzle. Dispersion powders of polymers having a low glass temperature tend to block and this destroys or reduces the dispersibility. By blocking is meaned adhesion between particles of the powder under conditions of low temperature and pressure (say 0.05 kg/cm² and 60°C), which adhesion affects the desired properties of the powder. It has been proposed to improve the dispersibility by considerably increasing the amount of protective colloid in the dispersion before it is atomised. The addition of extra protective colloid before the end of the polymerisation has been suggested. Furthermore it has been recommended, in order to reduce the tendency towards blocking, either to add inert substances to the dispersions before they are atomised or to introduce inert substances into the powders during drying. When a small quantity of an inert substance is added the surface of the substance is, however, completely covered by the powder, so that an effective reduction of the tendency towards blocking cannot be achieved.

This invention provides a process for the manufacture of a non-blocking dispersible powder of a vinyl acetate polymer or a copolymer of vinyl acetate and at least one ethylenically unsaturated compound, the polymer or copolymer having a glass temperature of 30°C or below (down to −25°C), which comprises polymerising vinyl acetate or a mixture of vinyl acetate and at least one ethylenically unsaturated compound in an aqueous dispersion to a monomer conversion within the range of from 80 to 90%, adding to the dispersion a polyvinyl alcohol having a viscosity within the range of from 3 to 13 cps (4% by weight aqueous solution at 20°C) and a saponification number of 60 to 255, completing the polymerisation, forming a powder from the dispersion by atomisation followed by drying, and adding an inert substance to the powder after it leaves the drier. If desired, an anti-foaming agent may be added simultaneously to the dispersion either with the polyvinyl alcohol or after completion of the polymerisation. Herein, a low glass temperature is understood to be a glass temperature of +30°C and below (down to −25°C). (Determination of the glass temperature, cf. Adhasion, 1966, 3, pages 97 to 100).

As polyvinyl alcohols with a saponification number of 60 to 255 it is possible to use water-soluble, partially esterified, for example, acetalised, polyvinyl alcohols or water-soluble saponification products of copolymers of a vinyl ester with at least one hydrophobic monomer that does not saponify under the conditions used to saponify the ester, for example vinyl chloride.

The polyvinyl alcohols preferably used in the process have a viscosity of 5 to 7 cps (4% by weight aqueous solution at 20°C) and a saponfication number of 115 to 168. The polyvinyl alcohol is preferably added in a quantity such that the product after drying contains about 0.5 to 4% by weight of the polyvinyl alcohol. This makes it possible to maintain higher concentrations of the dispersions employed during atomising without

SEE ERRATA SLIP ATTACHED

the atomisability thereof suffering. At the same time the good cold water solubility of the added polyvinyl alcohols effects rapid and good dispersibility of the powder obtained by the process.

Breakdown of the atomising nozzles occur after only a short operating period when polyvinyl alcohols of higher viscosity (25 cps, 4% by weight aqueous solution at 20°C, and above) are added to the polymerisation mixture after a monomer conversion of 80 to 90%, presumably because as a result of the higher viscosity of the polyvinyl alcohols the jet of liquid no longer breaks off completely. Small remnants of the liquid remain on the nozzles and these rapidly dry to give a film. Because the profile of the nozzle is affected a heavier residue forms, so that a deposit soon becomes visible, and this very rapidly grows into a projection. If this interfering factor is not rapidly removed, the drier is within a short time blocked through sheet formation. A reduction of the concentration of the initially introduced dispersion admittedly effects an improvement, but reduces the output of the drier.

When polyvinyl alcohols of a saponification number of above 255 are added to the polymerisation mixture after a monomer conversion of 80 to 90% difficulties also occur. On warming the dispersion the polyvinyl alcohol forms a jelly-like precipitate as a result of which breakdowns arise on atomising and conveying the dispersion. These defects can admittedly be reduced by strongly cooling the dispersion but this increases the viscosity of the dispersion, which makes it necessary to dilute it and hence results in a reduction of the drier output.

On dispersing the powders, foam formation can frequently be observed and in order largely to prevent this, anti-foaming agents may optionally be added during the polymerisation or subsequently. Suitable materials for this are, for example, silicone emulsions, combinations of silicone emulsions or conventional anti-foaming agents which are non-volatile under the particular working conditions. Such as gluconic acid or a water-soluble derivative of gluconic acid. A combination of a silicone emulsion with gluconic acid or water-soluble derivative of gluconic acid has proved especially successful.

It has furthermore proved appropriate to mix powdered inert substances that are capable of coating the surface of the powdered polymer particles of the spray dried dispersions, after it has left the drier, preferably in such quantities that the final product contains 5 to 20% by weight of the inert substance. Suitably inert substances are aluminium silicate, kieselguhr, colloidal silica gel, clays, gypsum, fine silicates, talc, cements and diatomaceous earth.

The inert substances will generally be added either during removal of the powders from the drier or in the powder separating chamber. It may, however, also take place in a second, separate process. The metering of the inert substance can in the former case, for example, take place by means of the metering screw of a vibrating chute or Polysius chute, which is closed off in an air-tight manner, by spraying in by means of an additional nozzle or by similar suitable measures.

Using the process according to the invention it is possible to obtain powders from polymers of low softening point which can be stored at higher temperatures and under pressure without the powder sintering together to give a solid block.

The following Examples illustrate the invention.

Example 1

150 parts by weight of vinyl acetate, 0.004 parts by weight of hydrogen peroxide and, as the emulsifier, 350 parts by weight of an 8% by weight aqueous polyvinyl alcohol solution having a saponification number of 140 mg KOH/g, are initially introduced into a stirred polymerisation apparatus having a reflux condenser, and heated. After polymerisation has started 45 parts by weight of vinyl acetate are added over the course of 3 to 4 hours. After completion of the addition 0.002 parts by weight of hydrogen peroxide are added, and the temperature after a short period rises to 80°C. The conversion of the vinyl acetate is now about about 85%. 15 parts by weight of a 20% by weight, aqueous polyvinyl alcohol solution, the polyvinyl alcohol having a viscosity (4% by weight aqueous solution at 20°C) of 3 cps and a saponification number of 100 mg KOH/g, are now added over the course of 15 minutes and 0.003 parts by weight of hydrogen peroxide are added after a further 10 minutes. After about one hour a temperature of 90°C to 93°C is reached and the reflux has completely ceased. The dispersion is cooled, adjusted to a solids content of about 33 to 35% by weight, and half of it is atomised. The atomisation takes place well and without breakdowns. The resulting powder is easily dispersible and has good storage stability under cool conditions. However, at temperatures of 50°C and a pressure of 0.05 kg/cm² blocking clearly occurs after 15 hours and on comminuting the lumps the dispersibility is reduced.

When atomising the second half of the above dispersion 10% by weight of aluminium silicate having an average particle size of less than 2 μ are added to the powder during the separation stage. The powder now obtained has good resistance to blocking in addition to the properties described above. The good dispersibility of the powder re-

mains unchanged even after 15 hours at 60°C and a pressure of 0.05 kg/cm².

EXAMPLE 2

(a) 500 parts of a 10% by weight aqueous polyvinyl alcohol solution (saponification number 140 mg KOH/g) to act as the emulsifier, 150 parts of vinyl acetate and 0.003 parts by weight of hydrogen peroxide are introduced into a stired polymerisation apparatus corresponding to Example 1 and are heated. After the polymerisation has started 300 parts of vinyl acetate are allowed to run in over the course of about 3 hours. At the same time a vigorous reflux is maintained, if appropriate by adding further quantities of hydrogen peroxide (0.0005 parts). After completion of the addition the temperature rapidly rises to 80°C. A monomer conversion of at least 80% is achieved.

20 parts by weight of a 20% by weight aqueous polyvinyl alcohol solution (viscosity 5 cps at 4% by weight of aqueous solution and 20°C, saponification number 140 mg KOH/g) are now added over the course of about 15 minutes, and 0.003 parts by weight of hydrogen peroxide are added. The temperature reaches 90 to 95°C in about 1 hour. Reflux has completely ceased. After half an hour the mixture is cooled, the dispersion is adjusted to a solids content of 33 to 35% by weight, and half of it is atomised. The material has good atomisability and an easily dispersible powder is produced which after grinding in an automatic mortar shows an air content of 1200 bubbles/cm² on spreading a film. After 15 hours at 50°C and 0.05 kg/cm² pressure the powder already has a clear tendency to block.

The second half is atomised as before, but 15% by weight of aluminium silicate having an average particle size of less than 2μ are admixed to the powder before it is separated. The powder now also withstands 50 hours at 60°C and 0.05 kg/cm² pressure without noteworthy blocking. The air content of a spread film is again high.

(b) 3 parts by weight of gluconic acid are added to the identical charge after running in the polyvinyl alcohol solution and after reflux has ceased. Thereafter the mixture is cooled as before, adjusted and atomised. The first half has, in addition to good dispersibility, 1,000 bubbles/cm² in a spread film after it has been ground in a Retsch mill, and the second half, containing 10% by weight of aluminium silicate with an average particle size less than 2μ, additionally has good resistance to blocking as in (a). The air content of the spread film, 950 bubbles/cm², is less than in (a).

(c) 4 parts by weight of a silicone emulsion are added to the charge as used under (b), instead of gluconic acid. After atomsing, the first half shows an air content of about 700 air bubbles/cm² in a spread film, and the second half, with 15% by weight of aluminium silicate of average particle size less than 2μ added, is non-blocking as in (b) and in a spread film shows an air content of 720 air bubbles/cm².

(d) 4 parts by weight of silicone emulsion are added to the charge as used under (b) in addition to 3 parts by weight of gluconic acid. After atomsing the first half shows an air content of 600 air bubbles/cm² in a spread film, and the second half containing 15% by weight of talc is non-blocking like (b) and (c) and shows an air content of 530 air bubbles/cm² in a spread film.

EXAMPLE 3

250 parts by weight of a 10% by weight aqueous polyvinyl alcohol solution (saponification number 140 mg KOH/g) to act as the emulsifier, 100 parts by weight of water 120 parts by weight of a mixture of 375 parts by weight of vinyl acetate and 125 parts of vinyl laurate, 0.008 parts of hydrogen peroxide and 0.003 parts by weight of potassium persulphate are initially introduced into a stirred polymerisation apparatus corresponding to Example 1, and heated. After a temperature of 70°C is reached the remaining monomer mixture and 100 parts by weight of water are allowed to run in over the course of 4 hours. The temperature is at the same time kept at about 80°C, optionally with replenishment of catalyst, and is raised to about 85°C half an hour after the end of the addition. The monomer conversion is now about 90%.

100 parts by weight of a 20% by weight aqueous polyvinyl alcohol solution (viscosity 13 cps at 4% by weight aqueous solution and 20°C, saponification number 80 mg KOH/g) are now added over the course of half an hour and this is followed by 0.004 parts by weight of hydrogen peroxide and 5 parts by weight of tributyl phosphate as an anti-foaming agent. The temperature rises to 90°C over the course of a further hour. The mixture is cooled, adjusted for atomising, and atomised. 10% by weight of aluminium silicate of average particle size less than 2μ are admixed to the powder after it issues. In addition to good dispersibility and a low air content of grinding the powder shows good resistance to blocking and remains free-flowing even after 15 hours at 50°C and 0.05 kg/cm² pressure.

EXAMPLE 4

A monomer mixture of vinyl acetate and dibutyl maleate is polymerised in dispersion in a stirred polymerisation apparatus corresponding to Example 1. 90% conversion is achieved at a temperature of 85°C when

the addition is complete. 2% by weight of polyvinyl alcohol (viscosity 5 cps at 4% by weight aqueous solution and 20°C, saponification number 165 mg KOH/g) are now added. After complete polymerisation the mixture is cooled, adjusted for atomising, and 1 to 2% by weight of gluconic acid as anti-foaming agent are added. The powder obtained on atomising has good dispersibility but moderate resistance to blocking. Good resistance to blocking is achieved by adding 20% by weight of gypsum ($CaSO_4 . 2H_2O$).

EXAMPLE 5

A mixture of vinyl acetate, vinyl chloride and vinyl laurate is polymerised as a dispersion in a stirred pressure autoclave at 65°C and at an initial pressure of 6 atmospheres. On reaching 90% conversion 2% by weight polyvinyl alcohol (viscosity 5 cps at 4% by weight aqueous solution and 20° C, saponification number 210 mg KOH/g) are metered into the autoclave. After completion of the polymerisation the pressure is released, and the mixture cooled, adjusted for atomsing and atomised. The resulting powder is easily dispersible but tends to block. A largely non-blocking powder is obtained after adding 5% by weight of kieselguhr.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a non-blocking dispersible powder of a vinyl acetate polymer or a copolymer of vinyl acetate and at least one ethylenically unsaturated compound, the polymer or copolymer having a glass temperature of 30°C or below (down to −25°C), which comprises polymerising vinyl acetate or a mixture of vinyl acetate and at least one ethylenically unsaturated compound in an aqueous dispersion to a monomer conversion within the range of from 80 to 90%, adding to the dispersion a polyvinyl alcohol having a viscosity within the range of from 3 to 13 cps (4% by weight aqueous solution at 20°C) and a saponification number of 60 to 255, completing the polymerisation, forming a powder from the dispersion by atomisation followed by drying, and adding an inert substance to the powder after it leaves the drier.

2. A process as claimed in claim 1, wherein the polyvinyl alcohol has a viscosity within the range of from 5 to 7 cps (4% by weight aqueous solution at 20°C) and a saponification number of 115 to 168.

3. A process as claimed in claim 1, wherein the polyvinyl alcohol is added in such a quantity that the dried powder contains about 0.5 to 4% by weight of the polyvinyl alcohol.

4. A process as claimed in any one of claims 1 to 3, wherein the polyvinyl alcohol is a water-soluble, partially esterified polyvinyl alcohol or a water-soluble saponification product of a copolymer of a vinyl ester and at least one hydrophobic monomer that does not saponify under the conditions used to saponify the ester.

5. A process as claimed in claim 4, wherein the polyvinyl alcohol is a water-soluble partially acetalysed polyvinyl alcohol.

6. A process as claimed in claim 4, wherein the polyvinyl alcohol is a water-soluble saponification product of a copolymer of a vinyl ester and vinyl chloride.

7. A process as claimed in any one of claims 1 to 6, wherein an anti-foaming agent is added to the polymerisation batch either simultaneously with the polyvinyl alcohol or after completion of the polymerisation.

8. A process as claimed in claim 7, wherein the anti-foaming agent is a silicone emulsion, gluconic acid or a water-soluble derivative of gluconic acid.

9. A process as claimed in claim 7, wherein the anti-foaming agent is a combination of a silicone emulsion and gluconic acid or a water-soluble derivative of gluconic acid.

10. A process as claimed in any one of claims 1—9, wherein the inert substance is aluminium silicate, kieselguhr, colloidal silica gel, a clay, gypsum, a finely ground silicate, talc, a cement of diatomaceous earth.

11. A process as claimed in any one of claims 1—10, wherein the inert substance is added in such a quantity that the finished product contains 5 to 20% by weight of inert substance.

12. A process as claimed in any one of claims 1—11, wherein the inert substance is added either during the removal of the powder from the drier or in the powder separating chamber.

13. A process as claimed in any one of claims 1—11, wherein the inert substance is added in a second, separate stage.

14. A process as claimed in claim 1, conducted substantially as described in any one of the Examples herein.

15. Non-blocking dispersible powders of polymeric materials whenever prepared by a process as claimed in any one of claims 1 to 14.

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